

INFLUENCE OF HEAT TREATMENT AND CARBON CONTENT ON THE STRUCTURE OF PURE IRON CARBON ALLOYS

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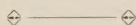
This investigation was carried out under the supervision of Professor E. D. Campbell, whose constant interest and valuable advice I gratefully appreciate. I also acknowledge the valuable suggestions and aid which Professor G. A. Lindsay and Professor C. Upthegrove gave during the course of the work.

Wm L. Fink



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INFLUENCE OF HEAT TREATMENT AND CARBON CONTENT ON THE STRUCTURE OF PURE IRON-CARBON ALLOYS

BY W. L. FINK AND E. D. CAMPBELL

Abstract

X-ray patterns were obtained from a series of pure iron-carbon alloys varying only in carbon content. Photomicrographic records were made of the identical surface used for X-ray work.

The changes in the alpha iron lattice, the presence of gamma iron lines, the changes in the gamma iron lattice, and the presence of carbide lines were all observed. Moreover, a body-centered, tetragonal structure, not previously observed, was found in high carbon, water-quenched steels. The observed facts were correlated with the carbon content and heat treatment.

HISTORICAL REVIEW

THE idea that crystals are built up by an orderly arrangement of minute particles was first proposed by Robert Hooke¹ (1) in 1665, and the possible arrangements for alum were shown. In 1801, Haüy (2) expressed the same idea, and developed the theory more in detail than Hooke had done. He named the particles from which the crystals are built: "Molécules Intégrant," and the elementary particles which combine to form these "Molécules Intégrant" he called "Molécules Élémentaires."

During the interval from 1801 until the advent of X-ray methods in 1912, the idea became firmly established and a theory completely worked out by Frankenheim (3), Bravais (4), Sohncke (5), Schoonflies (6), Fedorov (7), Barlow and Pope (8), and others, concerning the possible space lattices and point systems, according to which these minute particles could be arranged. It was shown that there were fourteen possible space lattices, and 230 point groups. There was, however, no way of determining the number of molecules in one structural unit, nor the absolute spacings.

¹The figures appearing in parentheses refer to the corresponding number in the bibliography appended to this paper.

A paper presented before the Winter Sectional Meeting of the Society, January 21 and 22, 1926, at Buffalo, N. Y. The work presented in this paper was done by W. L. Fink under the supervision of the late Professor E. D. Campbell, and submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

These determinations waited for the development of X-ray methods which were introduced by the well-known experiment of Friederick, Knipping and Laue (9, 10) in 1912. In the years immediately following, W. H. Bragg and W. L. Bragg (11) developed an X-ray spectrometer which was admirably suited to the investigation of large, well-formed crystals, and introduced a simple method of interpreting the X-ray data so obtained. The structure of a large number of crystals was worked out by this method. The kind of lattice, the actual dimensions, and the nature of the particles forming the lattice were all determined. The X-ray data confirmed the mathematically derived theory of space lattices, and point groups.

As important as these data were, they were, until the powder method was developed, limited to such substances as could be obtained in large, well-formed crystals. The powder method which was developed independently by Hull (12) and by Debye and Scherrer (13), made it possible to investigate the crystalline structure of a substance when it was in the form of a fine powder. This made X-ray methods applicable to the field of theoretical metallurgy. Naturally, the first step was the determination of the structure of pure metals. The principal workers in this field have been Hull, W. L. Bragg and McKeehan. Vegard, Debye, Scherrer, Bohlin, Kirchner, Bijl, Kolkmeijer, and others, have also contributed. A resumé of the work which had been done on the structures of pure metals up to 1922, together with references, has been written by A. W. Hull (14). A more recent (1924) and more complete list has been compiled by Wyckoff (15). Ewald (16) also gives a bibliography of work done on the structure of the elements.

The next step, the investigation of alloys, has little more than been begun, but some generalizations have been reached. Articles giving generalizations and theoretical explanations have been written by Jeffries and Archer (17), Bain (18, 19, 20, 21), Rosenhain (22), Tammann (23), Wever (24), and Davey (25). There is no good bibliography on X-ray investigations of alloys. Most of the alloys and series of alloys other than steel, which have been investigated, together with the names of the investigators, are appended to the bibliography at the end of this report.

There are different modifications of the powder method used

in the investigation of alloys. The Hull method, which is most widely used in this country, has been described by Bain (47), and Davey (48, 49, 25), and Blake (50). The Bohlin method, which was used for a part of the present investigation, was described by Seeman (51), Bohlin (52), Kirchner (30), and Lange (53). An application of the ionization chamber to the powder method has been described by W. H. Bragg (54), and by Owen and Preston (55). A modification of the latter method, which seems to be quite an improvement, has been very recently described by Soller (56).

In addition to the work carried on to determine the crystal lattices characteristic of the elementary metals and alloys, there has been a considerable amount of work done on crystal size and directional crystal orientation in worked and electrolytically deposited metals. Advances in this field prior to 1924 are well presented by Jeffries (78), and references are given to the original papers on the subject. A recent article which also gives references to original papers of other workers has been written by Clark, Brugmann and Heath (79).

INVESTIGATIONS ON STEEL

The pioneer work on steel was done by Westgren (57, 58, 59, 60) and those who worked with him. In the work reported in 1921 he used two samples of austenitic steel—a nickel steel and a manganese steel. The nickel steel had the following composition:

Nickel	25.2
Carbon	0.24
Manganese	0.50
Silicon	0.10
Phosphorus	0.047
Sulphur	0.010

The manganese steel had the following composition:

Manganese	12.1
Carbon	1.34
Silicon	0.52
Phosphorus	0.10

Both were water-quenched from 1000 degrees Cent. (1832 degrees Fahr.). Sharp lines were obtained which showed that these steels had a face-centered lattice, with 3.58 Angstrom units for the edge of unit cube in the case of the nickel steel, and 3.61 Angstrom units in the case of the manganese steel. An S. K. F.

bearing steel (carbon 1.25 per cent, and other elements not given) was also investigated in the pearlitic and martensitic conditions. No carbide lines were obtained. The annealed steel showed the lines characteristic of alpha iron. The martensitic steel had a body-centered structure with a cube edge of 2.88 Angstrom units. Finally, a hardened high speed steel (composition not given) was also investigated after quenching in oil from 1275 degrees Cent. (2325 degrees Fahr.). There were no gamma iron lines. The lines obtained were from alpha iron ($a = 2.86$ Angstrom units) and from the iron carbides. Tempering at 575 degrees Cent. (1067 degrees Fahr.) made no difference in the lines obtained.

In 1922 it was shown by Westgren that gamma iron had a different value for edge of unit cube in two samples of austenitic steels. The composition of one was 24.3 per cent nickel, 6.05 per cent manganese, and 1.18 per cent carbon, and the composition of the other was 25.2 per cent nickel and 0.24 per cent carbon. The values of unit cube were 3.64 and 3.56 Angstrom units, respectively. It was also shown that for a straight carbon steel the elementary cube of gamma iron was larger when the quenching was carried out from a higher temperature—1000 and 1100 degrees Cent. were the temperatures used. Work on two different samples also seemed to indicate that there was a change in the alpha iron lattice of the straight carbon steels with different carbon contents—the quantities of the other elements were not given. The result of an investigation of iron-carbide was also reported.

Franz Wever (61) published an article on the crystal structure of steel at about the same time that Westgren published his work, but he published in a journal which is not available, and the following facts concerning his work were obtained from the abstract which appeared in the *Physikalische Berichte*. For alpha iron, a was found to be 2.850 Angstrom units, and for gamma iron, a was found to be 3.56-3.60 Angstrom units. Cooling austenitic steel in liquid air was found to change part of the gamma iron to alpha iron. Tempering above 300 degrees Cent. was found to convert all of the iron to the alpha form.

Three other points in regard to steel had been published prior to the beginning of the present work. Jeffries and Bain (62) examined a sample of austenitic steel containing 13 per cent manganese and found that it had a face-centered cubic struc-

ture. Andrews (27) found that nonmagnetic nickel steel which had a face-centered cubic structure was partially changed to a body-centered structure by cooling for two hours in liquid air. Bain (63) found that an austenitic nickel steel spontaneously changed, so that after standing fifteen months it gave a pattern of fine-grained ferrite.

During the course of the present investigation, several articles on the structure of steel were published. Zorning (64) investigated a 1.10 per cent carbon steel and reached the following conclusions: Martensite consists of alpha and gamma iron. In troostite, sorbite, and pearlite the iron exists entirely in the alpha form. The gamma iron crystals do not seem to suffer distortion as long as they exist. The alpha iron crystals are probably distorted in martensite, but the distortion decreases as the structure approaches sorbite.

Franz Wever (65, 66, 67) published three articles—one on iron carbide, one on graphite and temper carbon, and one on the constitution of steel. He investigated a series of iron-manganese-carbon alloys. It was found that $a = a_0 + 0.00050 \text{ manganese} + 0.00645 \text{ carbon}$, where $a_0 = 3.578$, and manganese and carbon are expressed in atomic per cents. It was also found that the specific volume $v = 0.1246 + 0.0004 \text{ manganese} + 0.0041 \text{ carbon}$. From these data it was calculated that the carbon atoms in austenite are in the interstices of the iron lattice. He also did work on iron-carbon alloys, and concluded that carbon is not soluble in alpha iron under conditions of equilibrium. He concluded that the carbon in martensite is atomically dispersed, and held in the interstices of the alpha iron lattice.

Heindlhofer (68) in his investigation of hardened steel used three samples, compositions of which were given as (1) "carbon-free iron," (2) carbon 0.80 per cent, chromium 0.14 per cent, manganese 0.35 per cent, silicon 0.19 per cent, (3) carbon 1.31 per cent, chromium 0.12 per cent, manganese 0.24 per cent, silicon 0.17 per cent. A spectrometer with an ionization chamber was used. In the two martensitic samples the 3 1 0 planes were found to be closer together than in pure iron and the 2 1 1 planes were found to be farther apart than in pure iron. The difference in the per cent of the carbon made no difference in the positions of the lines. Tempering was found to make the lines more intense. The density of the specimens was determined experi

mentally and compared with the values computed according to different assumptions. He attempted to determine the structure of martensite on the basis of these determinations.

W. E. Williams (69) used both the Laue method and the powder method. The material used was a carbon tool steel (carbon 1.15 per cent, silicon 0.15 per cent, manganese 0.32 per cent, sulphur 0.006 per cent, phosphorus 0.032 per cent, tungsten 0.09 per cent, vanadium 0.05 per cent). A specimen quenched from 1100 degrees Cent. (2012 degrees Fahr.) in water at 10 degrees Cent. gave a Laue pattern which showed asterism. This was considered as an indication that the lattice was warped, or had an exceedingly fine-grained structure. A specimen which was quenched from near the solidus [1320 degrees Cent. (2408 degrees Fahr.)] showed a structure resembling austenite, but gave only alpha iron lines in a position which indicated a cube edge of 2.86 Angstrom units. The effect of tempering was determined by the Laue method. It was found that there was less scattered radiation from the tempered specimen, but that the radial pattern was not altered by tempering. This was considered as an indication that tempering does not produce recrystallization of the distorted crystals, and that the extreme hardness of martensite is not to be ascribed to this distortion.

Soller (56) used a piece of "ordinary commercial steel" in trying out his improved spectrometer. Little concerning steel can be obtained from this article, but it is interesting that there are more peaks than can be accounted for. It is unfortunate that Soller did not use a piece of steel that he knew something about.

Heindlhofer and Wright (70) investigated the effect of tempering hardened steel balls at various temperatures. Two different steels were used: (1) carbon 1.06 per cent, chromium 0.71 per cent, manganese 0.40 per cent, silicon 0.32 per cent, sulphur 0.015 per cent, phosphorus 0.020 per cent; (2) carbon 0.98 per cent, chromium 0.55 per cent, manganese 0.25 per cent, silicon 0.27 per cent, sulphur 0.018 per cent, phosphorus 0.014 per cent. These steels were quenched in water from different temperatures between 800 and 950 degrees Cent., and all showed a martensitic structure. All of the hardened specimens gave gamma iron lines in addition to the alpha iron lines. Different tempering temperatures were used, and the density and X-ray patterns were ob-

tained for each. These results indicated two changes. The first, which is the breaking down of the martensitic structure, is accompanied by an increase in density. The second, which takes place largely between 200 and 260 degrees Cent., is the transformation of the residual austenite, and is accompanied by a decrease in density. The higher the tempering temperature, the more intense were the alpha iron lines obtained.

Mathews (71) gave the results of experiments carried out by Bain, which showed that a larger amount of gamma iron was retained in chromium steel when it was quenched in oil from 830 degrees Cent. (1525 degrees Fahr.) than when it was quenched in water from the same temperature.

Bain (72) determined the temperature at which austenite decomposes for a number of different kinds of steel. Cold work was shown to have an effect similar to that of temperature elevation. Explanations were offered for the results obtained. An explanation was offered for the fact pointed out in the preceding paragraph.

OBJECT OF THE RESEARCH

Westgren's work on iron and steel indicated that there was probably a change in the alpha iron lattice with changes of carbon content. The principal object of this investigation was to determine the effect of carbon content and heat treatment on the space lattice of alpha iron in pure iron-carbon alloys.

Since there seemed to be no agreement among metallurgists concerning the presence of gamma iron in hardened and tempered steels, it seemed to be desirable to determine by the presence of gamma iron lines, whether or not gamma iron was present in the different samples used. It was also the purpose of this work to correlate the X-ray results with the microstructure.

X-RAY METHODS USED

On account of the difficulty of preparing suitable steel specimens of a known uniform structure, the Hull method did not prove satisfactory. The method which was used for the oil-quenched specimens was first proposed by Seeman (51), and worked out independently by Bohlin (52). The method which was used for the water-quenched and tempered specimens was suggested by the Seeman wedge spectrograph.

PRINCIPLE OF THE BOHLIN METHOD

In the Bohlin method the slit *A*, specimen *B*, and film (ECD) are all placed on the circumference of the same circle (Fig. 1). This means that the surface of the specimen must be curved. All of the rays which come through the slit and are reflected from the same planes, are brought to a focus on the film, because

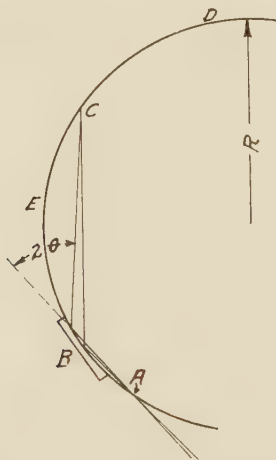


Fig. 1—Sketch Showing Principle of Bohlin Method. Slit, Specimen and Film are all on Circumference of Circle.

equal inscribed angles are subtended by equal arcs. A formula showing the relation between the angle Θ and the distance from the slit *A* to the line on the film (ECD), is easily worked out. The angle $ABC = CDA/2R$, and 2Θ is the supplement of angle ABC and is, therefore, equal to $ABC/2R$. This expression, together with Bragg's formula, $n\lambda = 2d \sin \Theta$, makes it possible to calculate the spacings (*d*) of the planes of atoms from the locations of the lines, and the wave length (λ) of the X-rays used.

PRINCIPLE OF THE WEDGE METHOD

In the Wedge method the edge of a wedge-shaped piece of lead or gold *J* is placed at the center of curvature of the film (OLNM), and the specimen *K* is placed within a few hundredths of a millimeter of the wedge (Fig. 2). The method is similar to the Hull method except that it is the width of the beam of

X-rays which is limited, instead of the size of the sample, and that the edge of the line is measured, instead of an estimated middle, to which a correction must be applied. The knife-edge or wedge extends beyond the specimen, so that the direct beam

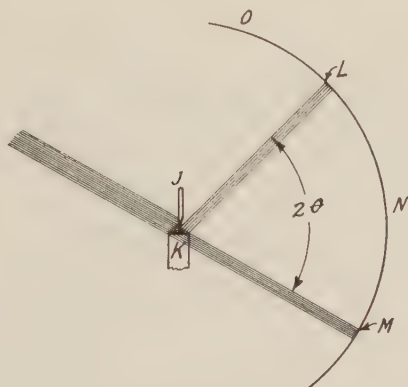


Fig. 2—Sketch Showing Principle of Wedge Method. Edge of Gold Wedge is at Center of Curvature of Film.

of X-rays strikes the film at *M*. Obviously $2\theta = LNM/R$, and the calculation is, of course, again made by use of the Bragg formula.

ADVANTAGES OF THE METHODS USED

Both of the methods used have advantages over the Hull method. The principal advantages arise from the fact that measurements are made to the edges of lines, the positions of which are not affected by the width of the slit, or depth of penetration of the X-rays, into the specimen. Thus these methods avoid the inaccuracies which are due to the size of the specimen and the varying depths of penetration into the specimen, which are inherent in the Hull method. Blake (50) carried out an extensive investigation of these errors in the Hull method, and outlines a procedure by which results can be quite accurately corrected. He discusses a correction proposed by Hadding (73), and suggests that a combination of Hadding's correction and his own would be more satisfactory than either alone. However, it is certainly more satisfactory to avoid the necessity of making such corrections.

The wedge method has the further advantage of making possible a photomicrographic record of the identical surface used for X-ray investigation.

X-RAY APPARATUS USED

Bohlin Method

Source of X-Rays. The X-ray tube was a molybdenum target, water-cooled, Coolidge tube manufactured by the General Electric Company for their X-ray diffraction apparatus. The filament was heated by means of three six-volt storage batteries,

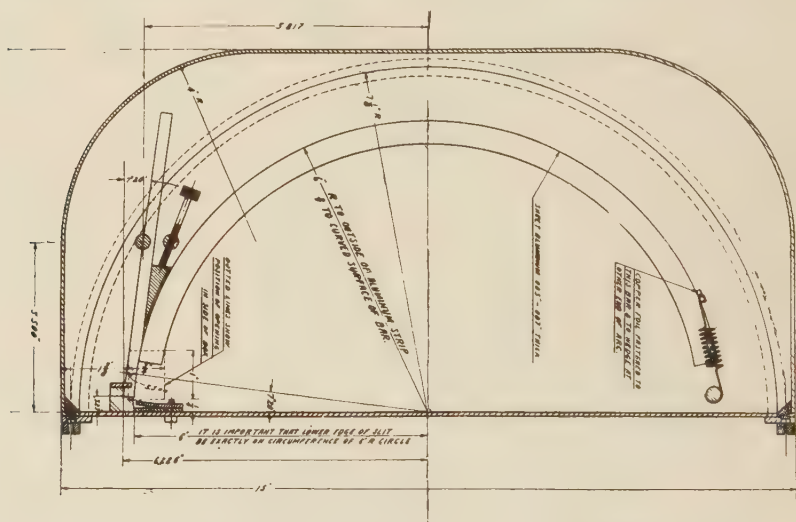


Fig. 3—Sketch of Cassette which was Used for Bohlin Method.

which were connected in series with a slide-wire resistance to control the filament current. The power for the tube was obtained as follows: A 220-volt direct current motor drove a 500-cycle alternating current generator, which was connected to the primary of a transformer. One end of the secondary was grounded, and the other connected to a kenotron. Connection was made from the kenotron to the filament of the tube. The voltage applied to the tube was regulated by means of a variable resistance in the generator field circuit. The tube was placed in a lead-covered box, and the lead, as well as the target of the tube, was grounded.

Cassette. The cassette was designed by the author and made by the Physics Department of the University of Michigan in their shops. The accompanying drawing (Fig. 3) shows the construction of the cassette as it was originally made. The piece of sheet

aluminum was subsequently replaced by a chromium oxide filter, which filtered out more efficiently the secondary iron radiation from the specimen. The cassette holds two specimens side by side—one a standard, and the other the bar under investigation. This was done to eliminate the difficulty due to the absence of a zero on the film, to eliminate the effect of changes due to

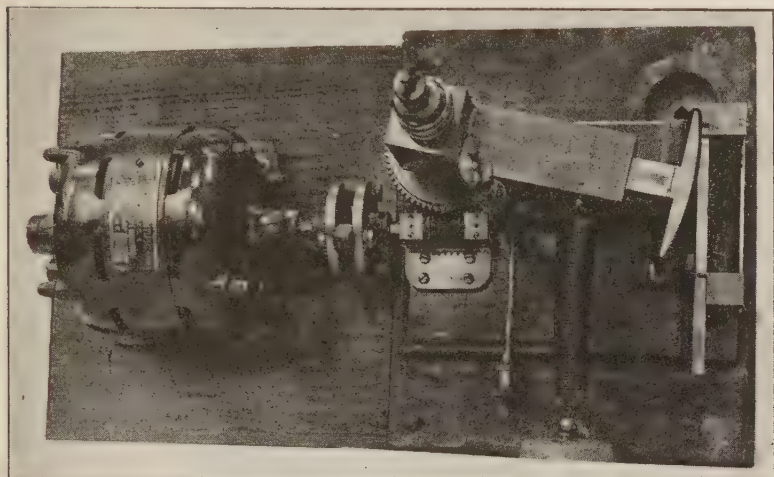


Fig. 4—Machine Used to Grind and Polish Curved Surface on Specimens Examined by Bohlin Method.

development, fixing, washing, and atmospheric conditions, and also to eliminate errors due to inaccuracies in the cassette.

Polishing Machine. It was found that better lines were obtained from a specimen with a polished and etched surface than from one which was merely ground. A polished and etched surface had the further advantage of allowing microscopic examination, although photomicrographs could not be taken on account of the impossibility of bringing all of the field into focus at once.

Consequently, the author designed the polishing machine, which is shown in Fig. 4. The polishing arm is actuated by two cams, one of which produces a lateral oscillation and the other a vertical. The frequency of the lateral oscillation is three times that of the vertical. There are four interchangeable polishing heads,—one covered with emery paper, one with canvas, and two with broadcloth. Three bars could be shaped at once with the emery cloth, and the final polishing done, one bar at a time, with

3F, 10F, and 65F alundum polishing powders, used in the order named on the three cloth covered polishing heads.

Measuring Apparatus

To measure the positions of the lines on the films a millimeter scale was first tried, and later a comparator. Both were

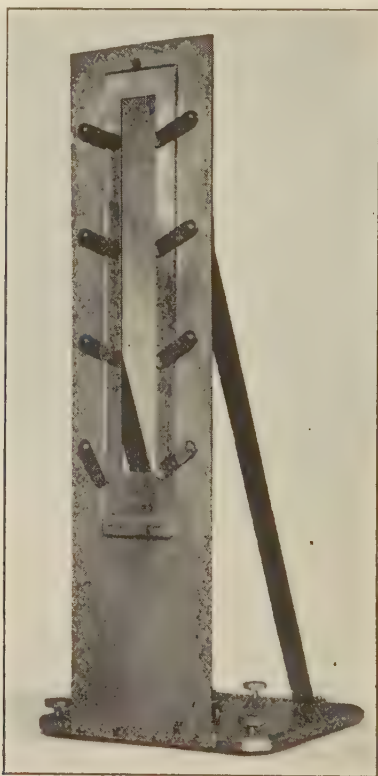


Fig. 5—Film Holder Used for Measuring Positions of Lines.

found to be unsatisfactory. The former was not accurate enough, and the latter magnified the lines too much and did not cover both sides of the film at once. All of the films were remeasured with the arrangement described below, and the values reported in this paper are those so obtained. The films were held vertically against a piece of plate glass in the apparatus shown (Fig. 5). Indirect lighting was used, i. e., light was reflected from a piece of unglazed white paper through the plate glass and the film.

The position of the lines was then determined by means of a cathetometer, which read directly to $\frac{1}{20}$ millimeter. The space between the film and the cathetometer was completely enclosed by means of heavy black cloth, to obviate the difficulties in meas-

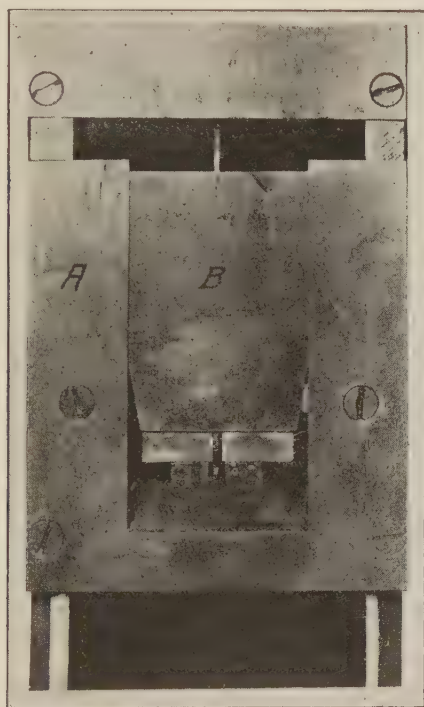


Fig. 6—Specimens and Knife-Edge in Position in Cassette for Wedge Method.

urement which arose when extraneous light was allowed to strike the lens of the cathetometer telescope.

Wedge Method

Source of X-Rays. The apparatus used for the wedge method was an X-ray diffraction apparatus. A detailed description of the apparatus is given in an article by Wheeler P. Davey (48). The outfit is compact and safe. The transformer is enclosed in a sheet metal cylinder, which is grounded. This cylinder is covered by a steel disk having a hole cut in the center, and having 15 radial guides for cassettes. A small metal cylinder which rests on this disk and fits the central hole, acts as a housing for

the tube, and a support for the slit system. The metal plate which covers the small cylinder acts as a support for the molybdenum target, water-cooled, Coolidge tube which is used in the apparatus. The filament is heated by a current induced in a few

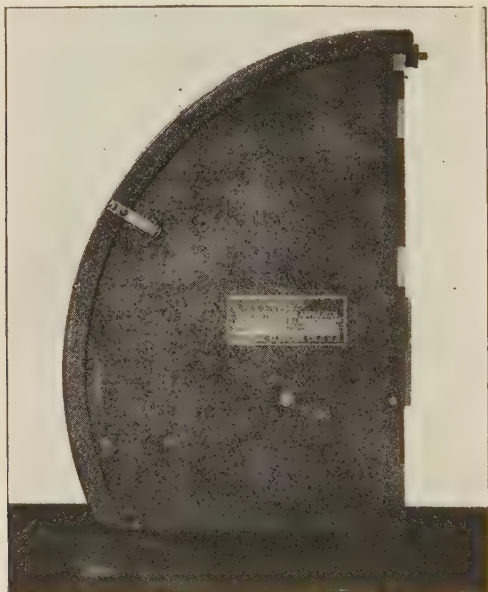


Fig. 7—Wedge Method Cassette.

turns on the high voltage end of the transformer. The tube rectifies its own current.

Cassettes. The cassettes which came with the apparatus were modified, as shown in Figs. 6 and 7. The specimen holders which were originally on the cassettes were removed, and the guide *A* was securely fastened to the front of the cassette with four screws. This guide was so placed that the edge of the gold wedge *B* was held at the center of curvature of the film. While changing specimens, the knife edge was removed and the guide served for part *C*, Fig. 8, which forced the specimens to the proper place.

Filter. In this case the filter used was the zirconium oxide filter, which is built in the cassette. It eliminates the secondary radiation from the specimen quite well, and also greatly reduces the beta doublet.

Measuring Apparatus. The same apparatus was used to measure the films as was used for the other method.

PROCEDURE

Preparation and Treatment of Materials Used

Preparation. During the school year 1922-23, the author, under the direction of Professor E. D. Campbell, worked out a

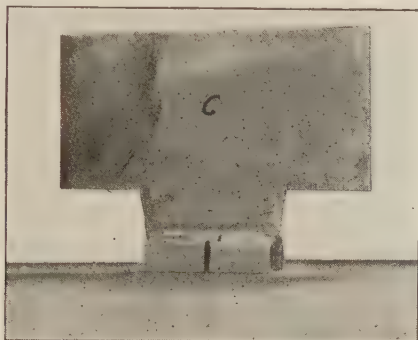


Fig. 8—Piece used to Mount Specimens as Shown in Fig. 6.

method (74) of preparing series of steels varying only in carbon content and having homogeneous structures. Briefly, the method consists in placing bars of different carbon contents, separated from each other, in a furnace at 950 degrees Cent. (1740 degrees Fahr.) in an atmosphere of hydrogen and allowing them to remain there until equilibrium was reached (seven days). The bars used for the oil-quenched specimens were prepared at that time, using bars 15 centimeters long and 6 millimeters square in cross section. The bars used for the water-quenched specimens were 15 centimeters long and 6.3 millimeters in diameter. These bars were prepared in essentially the same manner but with some improvements in technique (76, 77). The square bars were made from material furnished by the American Rolling Mill Company, and the round bars were made from material furnished by the Page Steel and Wire Company. The chemical compositions of the bars are given in Tables I and II, which show the atomic concentration of carbon as well as the per cent by weight.

Treatment of the Bars. The bars listed in Table I were suspended vertically in an electrically heated furnace which had been brought to the temperature from which it was desired to

quench (900 degrees Cent.). After holding at this temperature for one hour, the bars were quenched in oil at 20-30 degrees Cent. The temperature of the bars at the moment of withdrawal from the furnace was measured by means of a standard platinum-platinum-rhodium thermocouple, the bead of which was within

Table I

Atomic Concentration of Carbon and Per Cent by Weight of Bars Tested

IN5 Bar No.	Weight per cent Carbon	Milatoms Carbon per cubic centimeter
11	0.00	0.00
13	0.00	0.00
92	0.11	0.72
18	0.23	1.50
56	0.42	2.75
25	0.60	3.92
87	0.82	5.35
42	0.97	6.34
101	1.03	6.73
104	1.19	7.77
36	1.30	8.49

IN5 bars were made from Armco iron of the following composition:

	per cent		
Carbon	0.015		
Manganese	0.024	Silicon	trace
Phosphorus	0.005	Copper	0.042
Sulphur	0.023	Iron	remainder

2 or 3 millimeters of the bars under treatment. The upper half of the heating chamber in which the bars were suspended, consists of nickel-chromium wire gauze and is surrounded with charcoal, so that the bars may be maintained for any desired length of time without any sign of oxidation.

The bars listed in Table II were sawed nearly through at every centimeter of length, after stamping each section. The bars were heated in the same way as the previous set, but in this case they were heated to 940 degrees Cent., held for 40 minutes, and quenched in water at 2 degrees Cent. These bars were quenched horizontally, so that all sections would be the same. The sections were then broken apart and were tempered as described below.

Sections A were not tempered at all.

Sections B were sealed hermetically in an evacuated pyrex tube which was suspended above water in a round-bottom flask. The flask was fitted with a reflux condenser which was bent in

such a manner that the cold condensate could not strike the tube. The water was then boiled for two weeks continuously.

Sections C were treated in a similar manner. The liquid used in this case was meta cresol. The tube containing the specimens was placed in the liquid on pieces of porous plate, and a ther-

Table II
Atomic Concentration of Carbon and Per Cent by Weight of Bars Tested

OA1 Bar No.	Weight per cent Carbon	Milatoms Carbon per cubic centimeter
232	0.05	0.33
257	0.10	0.65
102	0.21	1.37
161	0.43	2.81
164	0.66	4.31
193	0.90	5.88
74	1.13	7.38
18	1.50	9.80

OA1 bars were made from Armeo iron of the following composition:

	per cent		
Carbon	0.010		
Manganese	0.028	Silicon	trace
Phosphorus	0.003	Copper	0.039
Sulphur	0.018	Iron	remainder

mometer placed with the bulb beside it. An air condenser was used in place of the water condenser which was used for sections B. The meta cresol was boiled for five hours. The boiling point was 203 degrees Cent. (400 degrees Fahr.) throughout.

Sections D were similarly tempered for five hours. Benzoic acid was used in this case, and the boiling point was 252 degrees Cent. (485 degrees Fahr.) throughout.

Sections E were heated in a like manner, in boiling glycerine for five hours. The initial boiling point was 284 degrees Cent. (543 degrees Fahr.). During most of the run the boiling point was 285 degrees Cent. (545 degrees Fahr.), but the glycerine gradually decomposed, and the boiling point rose near the end to 287 degrees Cent. (550 degrees Fahr.).

For sections F, mercury was used. The heating was for five hours. The boiling point was 348 degrees Cent. (660 degrees Fahr.) throughout.

Sections G were heated in an evacuated electric furnace to 500 degrees Cent. (932 degrees Fahr.). They were held between 500 and 510 degrees Cent. (932-950 degrees Fahr.) for one hour, and allowed to cool with the furnace.

Sections H were heated in the evacuated electric furnace to 800 degrees Cent. (1472 degrees Fahr.). They were held between 800 and 805 degrees Cent. (1472-1481 degrees Fahr.) for one hour, and allowed to cool with the furnace.

The material used as a standard for the oil-quenched specimens with the Bohlin method, was a decarburized (75) Armco iron bar, which had been oil-quenched from 900 degrees Cent. (1652 degrees Fahr.).

The oil-quenched decarburized Armco iron did not have a sufficiently fine-grained structure for the wedge method. Electrolytic iron furnished by the Bureau of Standards and decarburized (75) was tried and found to have too large a grain. To overcome this difficulty, small pieces of the electrolytic iron were cold-worked by means of a Brinell machine, and heated to 650 degrees Cent. (1202 degrees Fahr.) in an electric crucible furnace. After three such treatments the grain was sufficiently reduced.

Calibration of Thermocouple. The thermocouple, which was a Reichsanstalt standard platinum-platinum-rhodium thermocouple, was checked at the melting point of silver by placing a W-shaped piece of pure silver wire on the bead of the thermocouple, which was covered by a thin layer of asbestos, and then heating slowly in a silica tube furnace with a glass window in the end, until the wire melted. By heating sufficiently slowly, checks were always obtained to within 0.01 millivolt.

BOHLIN METHOD

Specimens. As was shown in the drawing of the cassette and in the photograph of the polishing machine, the full length bars (15 centimeters long) were used as specimens. Three of these bars were clamped in the polishing machine, and ground down with emery cloth. The bars were then polished one at a time. With a little practice, the bars could be taken down to the correct dimension and at the same time get a surface which had only a few light scratches. The curved surface was etched with 4 per cent alcoholic solution of nitric acid. The surface so prepared was satisfactory for X-ray examination, and was examined under the microscope.

Imperfections in the Cassette. There was found to be a great deal of general blackening on the film, due to secondary

rays from the back of the cassette. After discovering the cause of the blackening, the difficulty was easily remedied by placing a piece of lead foil between the copper foil and the back of the cassette.

The most troublesome defect was some inaccuracy in the parts which determined the location of the specimens, consequently the lines obtained were blurred when most of the curved surface of the specimen was used. Moreover, the two sides of the cassette were not the same. By using only two millimeters of the specimen, sharp lines were obtained.

To eliminate errors due to the inaccuracies in the cassette, and to obtain sharp lines, the following procedure was adopted and used for all work done by this method. The holder for the cassette was so adjusted that a length of about 2 millimeters at the middle of the polished arc was irradiated. The cassette was held in exactly the same position for all exposures. The cassette was calibrated by taking identical standard bars, and making several exposures with the bars in one position for half the exposure and interchanged for the other half. All of the films so obtained were identical and gave a calibration for the cassette.

Exposures. The first exposures were all made with 35 kilovolts across the tube, and 30 milliamperes of current. The length of exposure necessary to get the gamma iron lines to appear from oil-quenched specimens was at least thirty hours, and forty hours was found to be a more satisfactory exposure. When the General Electric Company diffraction apparatus was substituted, a holder was made so that the Bohlin cassette could be placed on that outfit. The current through the tube was 25 milliamperes and an exposure of 48 hours was used.

Films. Duplitized superspeed X-ray films were used. They were developed with X-ray developer and then fixed, washed and dried in the ordinary way. After drying, the emulsion on the back side was removed with a rubber policeman and nitric acid, which had been diluted with an equal volume of water. The film was then rinsed and dried.

Measurements. In measuring the positions of the lines on the films, the cathetometer and film holder were both set perpendicularly and the setting was checked by the use of a plumb-bob. The film was adjusted in the holder so that the film was

parallel to the cathetometer. This condition was determined by setting the vertical cross hair on the edge of the darkened portion of the film, and noting that it stayed there while the telescope was raised and lowered. The cross hairs in the cathetometer telescope were so adjusted that the vertical cross hair appeared to coincide with a thread which was used as a plumb line. When everything was in adjustment, the positions of the lines were read. The edge of the line farthest from the zero was measured in every case. For each line the intensity of the illumination was varied until the edge of that line could be most easily detected. Several readings were then taken on each line, and the average of the readings is the value used. It was found that the readings could be made more accurately in a darkened room, so that all except the first few were so made.

Calculation of Results. The calculation of the fractional change in the side of unit cube a was carried out by substituting in the equation

$$\frac{\Delta a}{a} = - \Delta \theta \sqrt{\frac{K^2 a^2}{\lambda^2} - 1}$$

which was obtained by differentiating the Bragg equation

$$\lambda = Ka \sin \theta$$

and substituting the finite increments Δa and $\Delta \theta$ for the differentials da and $d\theta$. This calculation obviously does not require the presence of a zero point to measure from. Heindlhofer (68) used this method of calculating the change in a . The calculation of the side of unit cube is a different matter, and an approximation can be had either by measuring the distance between the two lines, or the positions of the lines can be determined by comparison with lines from material of known crystal structure. The formula to be used in the former case is:

$$\cot \frac{L_1}{4R} = \frac{\frac{d_1}{d_2} - \cos \frac{a}{4R}}{\sin \frac{a}{4R}}$$

where L_1 is the distance from the slit to the line nearer the slit, R is the radius of curvature of the film,

$$\frac{d_1}{d_2}$$

the ratio of the spacings of the atomic planes involved, which can be calculated from the indices, and a is the measured distance between the lines. This equation was derived by dividing the Bragg equation for one line by that for the other, and solving for

$$\frac{L_1}{4R}.$$

The value of the side of unit cube calculated in this manner is not very accurate, for the inaccuracies in the cassette and changes in the film are not corrected or eliminated in any way. Moreover, the distance measured is relatively short, and a small absolute error is a larger percentage error than if the measurement could be made from the slit. However, such a calculation will give a close approximation. Kirchner (30) used this method in calculating part of his results.

THE WEDGE METHOD

The procedure which had to be followed in the Bohlin method, on account of the inaccuracies in the cassette, sacrificed two of the advantages of the method,—short exposures, and the use of specimens with coarse crystal grains. Moreover, to be compelled to always use the cassette in exactly the same position and calibrate it for that position, could not be considered entirely satisfactory. The preparation of the specimens was a slow process, and after they were prepared, photomicrographs could not be taken.

In view of these facts, the wedge method, which had not previously occurred to the author, was adopted. This method was quite satisfactory, except that the crystal grains had to be still finer than for the Bohlin method as it was used in this work.

Specimens. As was described in the preparation and treatment of the materials, the specimens used for the wedge method were 6.3 millimeters in diameter and 1 centimeter long. One end of the specimen was ground down 0.5 to 1.0 millimeters to avoid any surface change which might have occurred at the saw cut. That end was then polished on polishing discs, using 3F, 10F, and 65F alundum polishing powders. The specimens were etched with 4 per cent alcoholic solution of nitric acid, and photomicrographs were made.

Mounting the Specimens. The specimens were mounted in the cassette as shown (Fig. 6). First, modeling clay was placed at the front of the cassette and the specimen placed in it at approximately the correct place. The specimens were then forced into the clay by means of the piece C shown in Fig. 8. This piece was allowed to remain in place for a few minutes, to avoid hav-

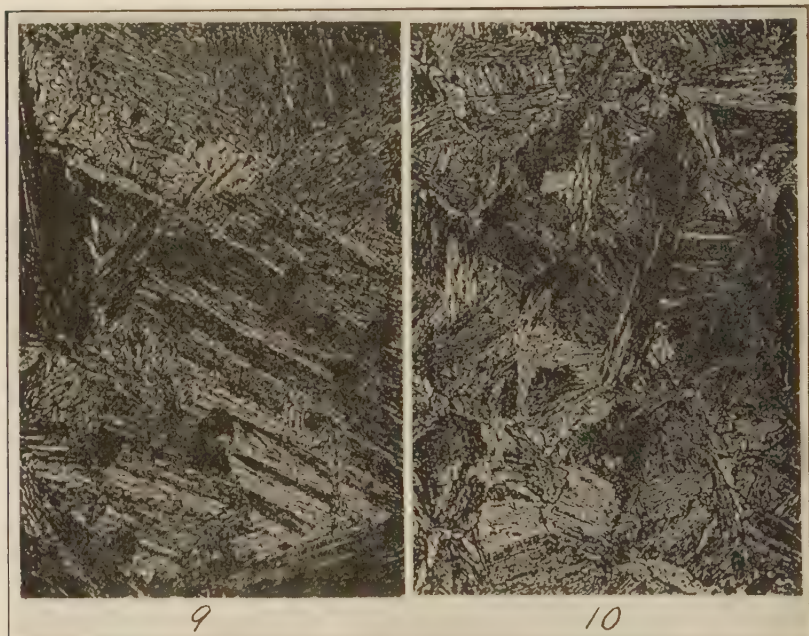


Fig. 9—Photomicrograph of Small Specimen of 0.05 Per Cent Carbon Steel Quenched in Large Volume of Ice Water. Fig. 10—Photomicrograph of Small Specimen of 0.10 Per Cent Carbon Steel Quenched in Large Volume of Ice Water. Specimens Etched with 4 Per Cent Alcoholic Solution of Nitric Acid. Magnification 500X.

ing the clay force the specimens up a little when it was removed. The knife-edge *B* was then put in place and the exposure started.

Exposures, Development and Measurement. The exposures, development and measurement of the films were carried out in a manner identical with that for the Bohlin method, except that no emulsion was removed from the film, because the paths of the X-rays were normal to the film.

Calculation. The calculations were carried out in essentially the same manner as for the Bohlin method. In this method, however, the angle between the original beam and the diffracted beam is a central angle and, consequently, $2\Theta = D/R$, where

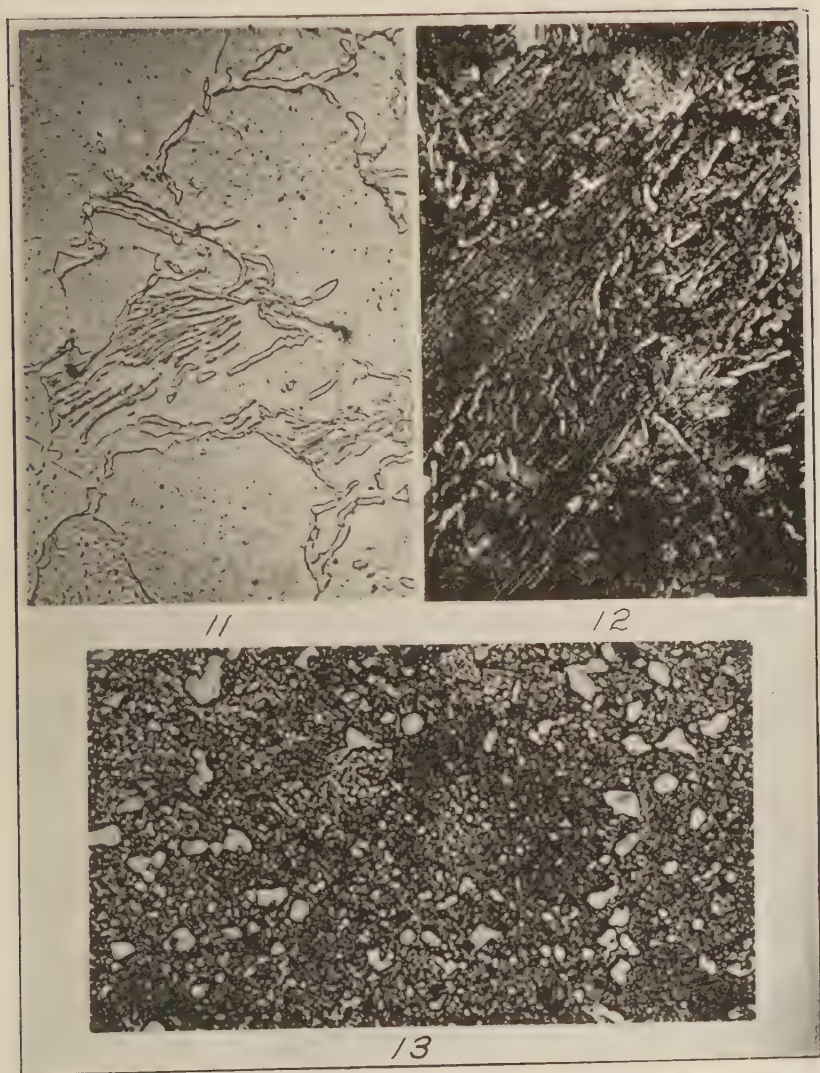


Fig. 11—Photomicrograph of 0.43 Per Cent Carbon Steel Annealed and Etched with a 4 Per Cent Alcoholic Solution of Nitric Acid. Magnification 500X. Fig. 12—Photomicrograph of 0.90 Per Cent Carbon Steel Annealed and Etched with 4 Per Cent Alcoholic Solution of Nitric Acid. Magnification 500X. Fig. 13—Photomicrograph of 1.13 Per Cent Carbon Steel Annealed and Etched with 4 Per Cent Alcoholic Solution of Nitric Acid. Magnification 500X.

D is the distance from the intersection of the direct beam with the film to the line. The spacing of the planes which give rise to a given line can be read directly by means of the scale which was furnished with the X-ray diffraction apparatus. The cor-

rections necessary to compensate for the changes in the length of the film can be determined from the standard lines. This procedure was used in determining the side of unit cube of gamma iron, and in identifying other lines.

RESULTS

Microstructures

Microscopic examination showed that the oil-quenched specimens were troostitic up to and including the 0.42 per cent car-

Table III
Measured Shift in the Alpha Iron Lines and the Calculated Per Cent

Carbon Content per cent	Treatment	Displacement lines in millimeters					Per cent changes in a				
		1 1 0	2 0 0	2 1 1	2 2 0	3 1 0	1 1 0	2 0 0	2 1 1	2 2 0	3 1 0
0.43	water- quenched	0.0	0.0	+0.1	+0.2	+0.4	0.0	0.0	+0.05	+0.13	+0.23
0.66	water- quenched	+0.1	-0.4	+0.2	+0.4	-0.7	+0.14	-0.39	+0.16	+0.26	-0.40
0.90	water- quenched	+0.1	-0.6	+0.3		-0.2	+0.14	-0.58	+0.23		-0.12
1.13	water- quenched		-0.4	+0.3	-0.2	-0.2		-0.39	+0.23	-0.13	-0.12
1.50	water- quenched	-0.2	-0.3	-0.1	-0.4	-0.5	-0.28	-0.29	-0.08	-0.26	-0.29
0.43	tempered at 100 C.	0.0	0.0	+0.1	+0.2	+0.4	0.0	0.0	+0.08	+0.13	+0.23
0.90	tempered at 100 C.		-0.2	+0.2	+0.2	-0.2		-0.20	+0.16	+0.13	-0.11
1.13	tempered at 100 C.		-0.3		+0.3	-0.2		-0.29		+0.29	-0.11

The + sign indicates an increased interplanar distance.
The -- sign indicates a decreased interplanar distance.

bon specimen. All specimens of higher carbon content showed a mixture of martensite and troostite. The largest amount of martensite was found in the 0.97 per cent carbon specimen. The water-quenched specimens were all martensitic—even the 0.05 and 0.10 per cent carbon specimens, as shown in Figs. 9 and 10. The structures of the tempered specimens are what would be expected. The structures of the annealed specimens are shown in Figs. 11, 12, 13.

X-Ray Results

Table III shows the measured shift in the alpha iron lines and the calculated per cent. Change in *a* for the water-quenched and the tempered specimens. The specimens not listed gave lines which were identical in position with those from the electrolytic iron standard. The oil-quenched bars all gave lines which were identical in position with those from the standard bar. Table

Table IV
Measured Gamma Iron Lines and Calculated Values of (a)

Carbon Content per cent	Treatment Degrees Cent.	Values of a calculated from lines		
		2 0 0	2 2 0	3 1 1
1.19	oil-quenched	3.56	3.56	
1.30	oil-quenched	3.56	3.56	
.90	water-quenched	3.590	3.586	3.605
1.13	water-quenched	3.610	3.615	3.605
1.50	water-quenched	3.612	3.598	3.608
.90	Tempered at 100	3.590	3.586	3.599
1.13	Tempered at 100	3.620	3.605	3.605

Table V
First Line Resolved

Carbon Content per cent	Treatment Degrees Cent.	First line resolved
0.11	oil-quenched	2 0 0
0.23	oil-quenched	2 2 0
0.42	oil-quenched	3 2 1
0.05	water-quenched	2 1 1
0.10	water-quenched	2 2 0
0.21	water-quenched	3 2 1
0.43	tempered at 203	3 3 2
0.43	tempered at 252	2 2 0
0.43	tempered at 285	2 1 1
0.43	tempered at 348	2 1 1
0.43	tempered at 500	2 1 1
0.43	annealed at 800	2 0 0
0.90	tempered at 252	3 2 1
0.90	tempered at 285	2 2 0
0.90	tempered at 348	2 1 1
0.90	tempered at 500	2 1 1
0.90	annealed at 800	2 0 0
1.13	tempered at 285	3 2 1
1.13	tempered at 348	2 1 1
1.13	tempered at 500	2 1 1
1.13	annealed at 800	2 0 0

IV shows the gamma iron lines which were intense enough to measure and the value of a calculated from each.

Table V gives the first line which was resolved, and where a sample is not listed, none of the lines were resolved. In explanation of this table, the X-rays used were not monochromatic, but consisted largely of the characteristic K-radiation of molybdenum, which is composed of four different wave lengths— a_1 (.708 Angstrom units), a_2 (.712 Angstrom units), β_1 (.631 Angstrom units), β_2 (.619 Angstrom units). The zirconium fil-

ter in the cassette absorbs most of the beta lines, although on some of the films the $K\beta$ lines are present. The lines given in the tables are due to the two $K\alpha$ rays (the alpha doublet). The wave lengths are close together and with well formed uniform grains they produce two lines close together, i. e., the doublet is resolved. Nonuniformity or distortion within the crystal grains causes these two lines to widen and merge, i. e., the doublet is not resolved.

There are two points not included in the tables which are important. The first is that 1.13 per cent carbon steel specimens tempered at 500 degrees Cent. (932 degrees Fahr.) and annealed at 800 degrees Cent. (1472 degrees Fahr.) gave a large number of iron carbide lines. No other films showed any carbide lines.

The other result which was not included in the tables was the appearance of new lines corresponding to a body-centered tetragonal lattice. The 0.90 per cent carbon water-quenched specimen gave 211 and 110 lines which were widened considerably on the short wave length side. The 1.13 per cent carbon water-quenched specimen showed this widening on all of the lines, but the 1.13 per cent carbon specimen tempered at 100 degrees Cent. (212 degrees Fahr.) did not. The 1.50 per cent carbon specimen showed new lines which corresponded to a body-centered tetragonal lattice having an axial ratio of 1.06. These lines were at approximately the same position as the short wave length edge of the excessively wide lines just mentioned.

DISCUSSION OF RESULTS

A point to be kept in mind in considering the results obtained is that all measurements are made to the long wave length edge of the lines. Therefore, if the lattice were not uniform throughout the specimen, the measurements would give the dimensions of those regions which have the smallest interplanar spacings, and those regions which have a greater spacing would simply cause the line to widen out on the short wave length side. Moreover, if the material consisted of lattices of different sizes, and a relatively small amount of the smallest one was present, the edge to be measured would be faint and difficult to measure.

Oil-Quenched Specimens

The characteristics of the lines were those which it has just been pointed out would exist if the lattice were not uniform. The

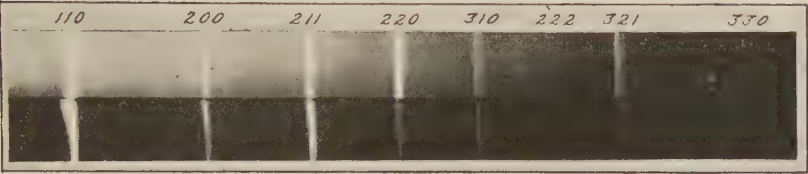


Fig. 14—X-Ray Pattern from 1.13 Per Cent Carbon Steel Annealed. Upper Lines Are from Electrolytic Iron Standard. Unidentified Lines Are Due to $K\beta$ Rays. The Lower Lines Are Due to the Steel. The Many Faint Lines Are Due to the Carbides.

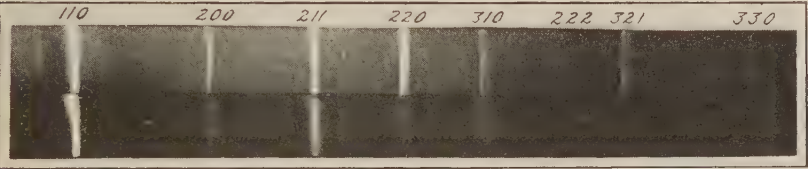


Fig. 15—X-Ray from 1.13 Per Cent Carbon Steel Tempered at 203 Degrees Cent. Upper Lines Are from Electrolytic Iron Standard. The Lower Lines Are from the Steel. Note the Absence of Resolution of the Lines, and Absence of Gamma Iron Lines.

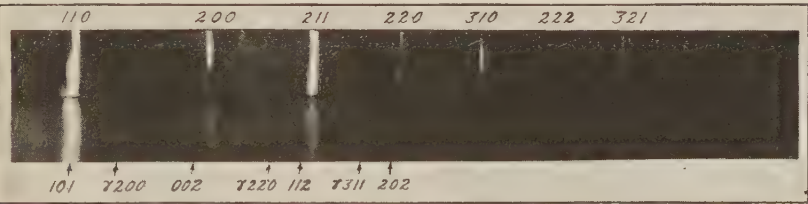


Fig. 16—X-Ray Pattern from 1.30 Per Cent Carbon Steel Quenched from 950 Degrees Cent. in Ice Water. Upper Lines Are from Electrolytic Iron Standard. Unidentified Lines Are Partly Due to the $K\beta$ Rays, and Partly Due to Surface Changes of Specimen which Were Eliminated by Repolishing. The Lower Lines Due to the Steel Are Partly Alpha Iron Lines as Are Those of the Standard, Partly Gamma Iron Lines as Indicated, and Partly Due to a Body-Centered Tetragonal Lattice, Having an Axial Ratio of 1.06.

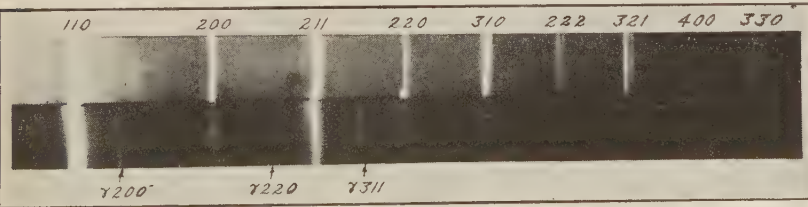


Fig. 17—X-Ray Pattern from 1.13 Per Cent Carbon Steel Quenched from 950 Degrees Cent. in Ice Water. Upper Lines Are from Electrolytic Iron Standard. Note Broad Lines from Steel Which Correspond to Body-Centered Tetragonal Lattices Having Axial Ratios All the Way Between 1.06 and 1 (Body-Centered Cubic).

locations of the lines were the same within experimental error for all of the steels of this series and decarburized ingot iron. This would indicate that some of the lattice at least was the same as that of pure alpha iron. The fact that the lines widened out

on the short wave length side seems to be most easily and logically explained by assuming that some parts of the lattice were dilated. The greater the broadening, the more lines there were in which the doublets have merged into one line. Therefore, the number of lines not resolved serves as a rather delicate indicator of the amount of dilation up to 0.60 per cent carbon, where none of the lines were resolved. Above that, the intensity and definition of the lines give an indication of the extent of the dilation. Other factors, such as mechanical strains, and a fine crystalline structure, may enter into the problem, but they are probably minor factors, or the lines would widen out on both sides.

Gamma iron lines did not appear until the carbon content had reached 0.97 per cent, and they were quite weak even for the specimens with higher carbon contents. The value of a for gamma iron in these specimens was found to be 3.56 Angstrom units. Although this determination by the Bohlin method with such weak lines was in all probability not as accurate as the ones made by the wedge method, it was certainly accurate enough to show that the lattice did not have the same dimensions in the oil-quenched and the water-quenched specimens.

Water-Quenched Specimens

For the 0.05, 0.10, and 0.21 per cent carbon specimens the results indicated that part of the lattice still had the same dimensions as that of pure iron. With increasing amounts of carbon, the per cent of the lattice which possessed the same dimensions as that of pure iron became less and less, and, consequently, the edge to which measurement was made became less and less distinct. In the 0.43 per cent carbon specimen there was none, or only little of the lattice of the original dimensions. Consequently, measurement showed the lines to be in slightly different positions. The shift of the line is then a criterion by which to judge the extent of the lattice dilation when none of the lines are resolved. There are, however, certain disturbing factors.

The specimens with 0.66 per cent or more of carbon contained gamma iron. For the 0.90 per cent carbon steels, both water-quenched and tempered at 100 degrees Cent., the median of the values obtained for the length of the side of unit cube was 3.59 Angstrom units (see results). The lattice dimensions seemed to be larger and nearly constant for the two water-quenched speci-

mens of higher carbon content, as well as for the 1.13 per cent carbon specimen tempered at 100 degrees Cent. The median of the values obtained was 3.608 Angstrom units.

This would mean that the spacings of the 4 0 0 planes would be 0.898 to 0.903 Angstrom units, whereas the 3 1 0 planes of electrolytic iron were found to have a spacing of 0.905 Angstrom units. In other words, as soon as the 4 0 0 line became intense enough to see, it made the 3 1 0 line appear to be at too great an angle, and indicated a contraction in the alpha iron lattice which did not exist. There is, however, a more serious difficulty in interpreting the changes in the positions of the alpha iron lines.

As was stated in the descriptions of the films, the lines on the film obtained from the 1.50 per cent carbon specimen could be accounted for by the presence of a body-centered tetragonal lattice with a value of a about 0.28 per cent smaller than that of alpha iron, and a value of c 1.06 times that of a . This would mean that as soon as any line from this lattice is intense enough to be seen, the corresponding line of the alpha iron pattern will seem to indicate a contraction in the alpha iron lattice. This explains the fact that the 2 0 0 and 3 1 0 lines are displaced to the long wave length side with the 0.66-0.90 per cent carbon specimens, and the 2 0 0, 2 2 0, and 3 1 0 lines are displaced in that direction with the 1.13 per cent carbon steel. In the case of the 3 1 0 lines, there are two factors, so that even though both are weak, the effect is noticeable.

It should be borne in mind that all the specimens of this series are martensitic and that the changes in the X-ray patterns are, therefore, due to the amount of carbon present in the same metallographic constituent. As the carbon content increased, the following changes took place in the iron lattice. At first there was a dilation of a part of the body-centered alpha iron lattice. Then the part of the lattice which was dilated, as well as the extent of the dilation, gradually increased. Finally, no noticeable quantity of the alpha iron lattice remained undilated. Further increase in carbon content caused the retention of part of the iron in the gamma form (face-centered cubic lattice), and probably a further dilation of alpha iron. Shortly after this, a new lattice made its appearance—the body-centered tetragonal lattice previously mentioned. The gamma iron lattice was also

somewhat dilated. Further increase in the carbon content increased the amounts of this body-centered tetragonal lattice. The body-centered tetragonal lattice did not seem to be of uniform dimensions in the 0.90 and 1.13 per cent carbon specimens, but did seem to be quite uniform in the case of the 1.50 per cent carbon specimen.

Tempered Series

Since the tempering process has the effect of agglomerating the carbides, it would be expected that on tempering, the changes described above would take place in the reverse sense. This is exactly what did take place. Tempering at 100 degrees Cent. caused a disappearance of almost all of the last component to make its appearance—the body-centered tetragonal lattice. Tempering at 203 degrees Cent. caused the disappearance of all the gamma iron lines, except in the case of the 1.13 per cent carbon steel, where they were quite faint; and also caused some of the alpha iron lattice to assume the dimensions of the lattice of pure iron. Higher tempering temperatures caused more and more of the lattice to return to the dimensions of a pure iron lattice. The lower the total carbon, the more complete the change at a given temperature. Specimens *E* tempered at 285 degrees Cent. bring out this point clearly. With 1.13 per cent carbon steel, the 3 2 1 line was the first to be resolved, while the 0.90 per cent carbon specimen showed partial resolution of the 2 1 1 line, and the 0.43 per cent carbon specimen gave good resolution of the 2 1 1 line. It was only on the annealed specimens that the effect of the carbides on the alpha iron lattice was completely eliminated.

An interesting and not easily explained fact is that iron carbides do not give any carbide lines when they are precipitated in sufficiently large particles to be easily seen at 500 diameters magnification. Even the annealed specimens with 0.43 and 0.90 per cent carbon did not give strong enough lines to enable one to state definitely that they existed. The 1.13 per cent carbon specimen did give carbide lines, but they were weak. It may be that longer annealing, or annealing at a higher temperature, would cause these lines to appear on the films from the other specimens.

The results obtained for the tempered specimens assist in explaining the results obtained for the oil-quenched specimens. The results obtained for the oil-quenched specimens were the same as would be expected from specimens which had been water-

quenched and tempered at a temperature a little lower than 200 degrees Cent. The relatively slow cooling during oil quenching would account for such results.

Possible Explanations of Previously Observed Facts

W. E. Williams (69) makes an interesting statement in regard to a steel quenched from 1320 degrees Cent. (2408 degrees Fahr.). "The structure is a cube-centered lattice, the cube side being 2.86 Angstrom units. There was no trace of any face-centered lattice lines. The steel thus, despite its appearance under the microscope, is in the alpha state." The steel under consideration was of the following composition: carbon 1.15 per cent, silicon 0.15 per cent, manganese 0.32 per cent, sulphur 0.006 per cent, phosphorus 0.032 per cent, tungsten 0.09 per cent, vanadium 0.05 per cent. It does not seem likely that after quenching such a steel from 1320 degrees Cent. (2408 degrees Fahr.) the iron would all be in the alpha state. Extending the results which have just been presented, it would seem that such a treatment might produce large amounts of the body-centered tetragonal structure. Considering the fact that the method used by Williams brought only one line into focus and gave diffuse lines for the others, he may have obtained a single broad line in place of each pair of lines which should have been obtained if all the structure had been body-centered tetragonal.

The author, while working for his master's degree, found that the modulus of elasticity of steel was lowered by drastic quenching, and that it was then raised considerably by tempering at 100 degrees Cent. This can now be explained by the appearance and disappearance of the body-centered tetragonal lattice.

The improvements in other physical properties caused by tempering at 100 degrees Cent. may be due in a large measure to the disappearance of the body-centered tetragonal lattice.

Future Work Indicated by Results

It seems that an investigation of high carbon pure iron-carbon alloys quenched at various temperatures between the A_1 point and the solidus, should give much information concerning the structure of steel and the changes which take place during heat treatments.

Work similar to that described in this thesis, but using series

of steels with different alloying materials in each series, should give much information concerning the effect of these elements on the structure of alloy steels, and help to interpret and predict their properties.

It would also be interesting to get diffraction patterns from steel at different temperatures, and thus determine whether the body-centered tetragonal lattice is a stable structure at any temperature, or whether it is a metastable transition structure which is encountered only in quenched steel. Such an investigation should bring out other important data.

CONCLUSIONS

The conclusions which were reached as a result of this investigation of pure iron-carbon alloys are summarized below.

1. Changes in the dimensions of the minimum alpha iron lattice (body-centered cubic) which take place during heat treatments are small (0-0.3 per cent approximately) and are a function of the carbon content and heat treatment. The side of unit cube increases slightly as the carbon content increases, but the change is not uniform throughout the lattice.

2. The gamma iron lattice (face-centered cubic) also changes with carbon content and heat treatment. The higher the carbon content and the more drastic the quench, the larger the size of unit cube. The range of values of a encountered in this work was from about 3.56 to 3.608 Angstrom units.

3. With drastic quenching of eutectoid and hypereutectoid steels, there is formed a crystal structure which has not been previously described, and which seems to be a body-centered tetragonal structure. The body-centered tetragonal lattice is not uniform with the lower carbon contents, but with higher carbon contents the lattice becomes fairly uniform. With the 1.50 per cent carbon specimen the value of a was 2.85 Angstrom units and the value of c was 3.02 Angstrom units.

4. The body-centered tetragonal lattice is less stable at low temperatures than the gamma iron lattice. The body-centered tetragonal lattice disappears on tempering at 100 degrees Cent., while the gamma iron does not disappear until 200 degrees Cent. is reached, and in the case of the 1.50 per cent carbon specimen it had not entirely disappeared then.

5. The relative quantities of the three kinds of lattices which

are produced by quenching are functions of the carbon content and the rate of cooling.

6. Carbides, for some unknown reason, do not in general give lines on the film. By annealing the high carbon steels, carbide lines are obtained. Thorough annealing or spheroidization might cause them to appear with lower carbon contents.

ACKNOWLEDGMENT

The author heartily thanks the General Electric Company for the two-year tenure of a Charles A. Coffin Fellowship which made this research possible.

INVESTIGATIONS ON ALLOYS OTHER THAN STEEL*

Iridosmium.....	Aminoff and Phragmen	(26)
Iron-nickel	Andrews	(27)
Iron-cobalt	Andrews	(27)
Copper-zinc	Andrews	(27)
Cu ₂ Zn ₃	Beeker and Ebert	(28)
Mg ₃ Al ₂	Beeker and Ebert	(28)
NiAl	Beeker and Ebert	(28)
CuAl ₂	Beeker and Ebert	(28)
CuAl	Beeker and Ebert	(28)
Ni ₃ W	Beeker and Ebert	(28)
Cu ₃ Al	Beeker and Ebert	(28)
Copper-aluminum.....	Jette, Phragmen, and Westgren	(29)
Copper-gold	Kirchner	(30)
Copper-nickel	Lange	(31)
Copper-gold	Lange	(31)
Silver-palladium	McKeehan	(32)
Silver-gold	McKeehan	(32)
Palladium-hydrogen	McKeehan	(33)
Palladium-hydrogen	McKeehan	(34)
Palladium-hydrogen	Yamada	(35)
Iron-nickel	McKeehan	(36)
Copper-zinc	Owen and Preston	(37)
Copper-aluminum	Owen and Preston	(38)
Aluminum-magnesium	Owen and Preston	(38)
Copper-nickel	Owen and Preston	(38)
Iron-silicon	Phragmen	(39)
Copper-nickel	Sacklowski	(40)
Tungsten-molybdenum	Van Arkel	(41)
Silver-gold	Van Arkel	(41)
Copper-aluminum	Westgren and Phragmen	(42)
Copper-zinc	Westgren and Phragmen	
Copper-zinc	Westgren (43) and Westgren and Phragmen	(44)
Copper-aluminum	Westgren (43) and Westgren and Phragmen	(44)
Silver-zinc	Westgren (43) and Westgren and Phragmen	(44)
Silver-cadmium	Westgren (43) and Westgren and Phragmen	(44)
Gold-zinc	Westgren (43) and Westgren and Phragmen	(44)
Silver-tin	Westgren (43) and Westgren and Phragmen	(44)
Silver-aluminum	Westgren (43) and Westgren and Phragmen	(44)
Heusler-alloys	Young	(45)

*The figures in brackets have reference to the figures to the list of references which follows:

Zinc-aluminum	Phebus and Blake (46)
Lead-tin	Phebus and Blake (46)
Chromium and Nickel.....	Phebus and Blake (46)
Aluminum-nickel	Phebus and Blake (46)

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Discussion of Paper

E. C. BAIN: I would compliment Dr. Fink upon the excellent X-ray patterns which he has made from which to compute the atomic spacings in martensite. In order to amplify what he has said and perhaps to make it more clear what the significance of the work is, I beg to repeat what I have offered before in lectures.

In the first place gamma iron solid solutions are a face-centered cubic arrangement of atoms with cube edge 3.60 Angstrom units in length. Such a cubic arrangement is at once a tetragonal body-centered arrangement of atoms with the base edge 2.54 Angstrom units in length and the vertical edge 3.60 Angstrom units in height. Or, as is usually designated, body-centered tetragonal with axial ratio 1.414 ($\sqrt{2}$). Now alpha iron is body-centered cubic with base edge 2.86 Angstrom units in length. The process, then, of the allotropic change so far as crystal structure is concerned, is merely the flattening or upsetting of the space lattice from 3.60 Angstrom units to 2.86 Angstrom units in height and the resulting widening of the unit crystal base to 2.86 Angstrom units from 2.54 Angstrom units. In such a process, as may be seen in this figure, the tetragonal axial ratio is changed from 1.414 to unity. (Fig. 1).

But let us assume that the forces which bring about this change in atomic spacing when the iron or steel is cooled below the transformation temperature

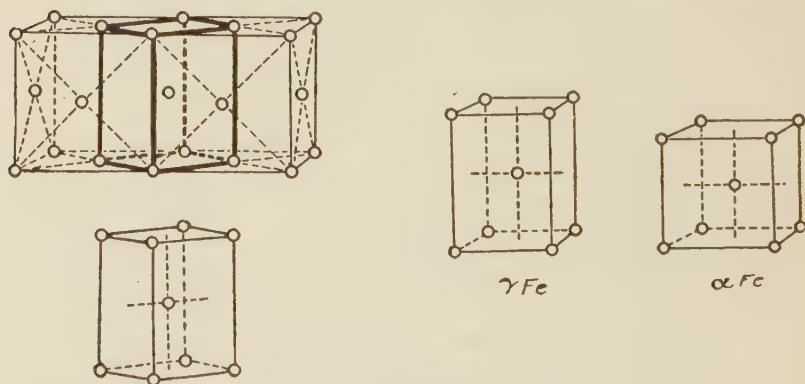


Fig. 1—The Relation of the Atomic Arrangement in Austenite to the Arrangement in Ferrite.¹

are greatest when the atoms are farthest from equilibrium position and gradually become less as the atoms reach the final position. (As though they were held by springs). Or suppose that the atoms themselves became more sluggish as the temperature drops and are more reluctant to assume the final exact position. Either assumption is not difficult to make and would imme-

¹"The Nature of Martensite," Edgar C. Bain, New York Meeting, American Institute of Mining and Metallurgical Engineers, February, 1924.

diately explain why the final condition in martensite does not exactly correspond with *perfectly* cubically-crystallized alpha iron. Now the inference is that, if the atoms do change by some such shift as we have pictured, then the final state reached in martensite which does not permit equilibrium, would be slightly tetragonal.

If one could have the whole of a large number of grains pass simultaneously through the allotropic change slowly, and could view the X-ray pattern as the change transpired then he would see a movement of the diffraction lines as shown in this chart (Fig. 2). Some of the single lines in either system divide in the tetragonal intermediate condition and reunite differently in the other form.

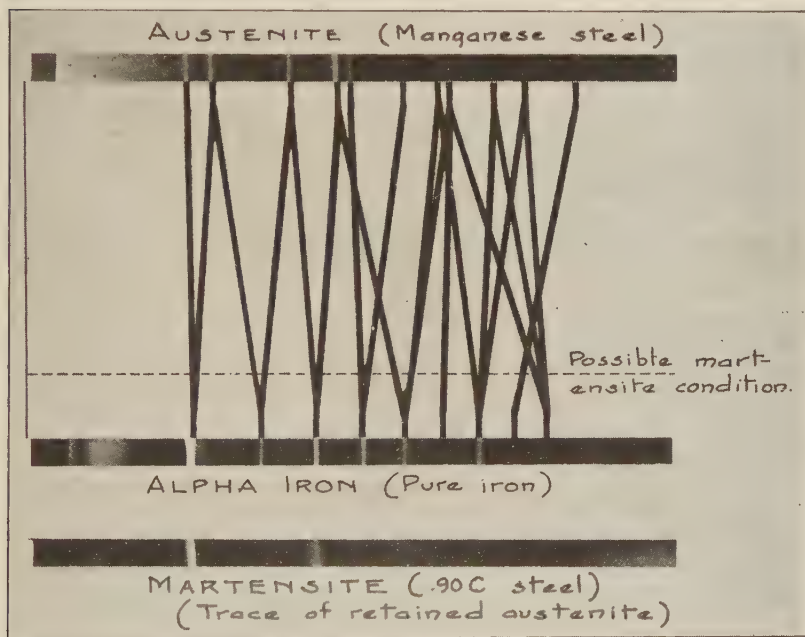


Fig. 2—Ideal Diagram of the X-ray Pattern Change Accompanying the Change from Austenite to Ferrite (+ Carbide).

The disturbance in the pattern at a slight departure from alpha iron is somewhat like our patterns of freshly quenched martensite showing broadened and doubled bands. Hence it may well be that in martensite the allotropic change is arrested just short of perfect crystallinity due to the rigidity of the atom structure at the low temperature of martensite formation.

I doubt greatly that one should attempt to assign an actual ratio to the axes in martensite. There could scarcely be a great preponderance of the tiny grains which would stop their internal atomic reorganization at a specific point,—the figure given by Mr. Fink then represents a statistical maximum in the distribution.

Furthermore, that this tetragonal condition—a stopping point of allotropic change—contains in it the essence of hard martensite must not be assumed, for when specimens are reheated it appears that restoration is established to the cubic condition of alpha iron at about 100 degrees Cent. *without any sacrifice in hardness.*

This knowledge, while not establishing, in any sense, a simple explanation of hardness in quenched steel marks certainly an advance in our lines of attack upon heretofore unknown ground. It is a step forward in our sincere struggle to determine the nature of martensite and to replace, as advancement permits, mere names with definite knowledge.

H. M. BOYLSTON: I wondered as I heard Mr. Fink and Mr. Bain, whether our old friend *beta* iron had risen once more from the grave where some have tried to bury it. It begins to look to me as if the X-ray spectrometer is going to show a crystallographic change—an intermediate change—between gamma and alpha iron. Even the stereopticon¹ took an unfair advantage of the situation and drew a nice bright curve through Mr. Bain's lantern slide, which might be considered a first approximation of a plane through martensite. Although I have not studied these data at all closely, it looks to me as if we are getting closer to an explanation of what martensite is, and to the reason for the critical point commonly known as A_2 . Whether we should call it an allotropic change and whether we should dignify it with the name of beta iron may have to wait a little longer. I thank you.

Author's Reply to Discussion

Mr. Bain in his discussion called attention to the generally recognized geometrical fact that the body-centered cubic and face-centered cubic lattices are special cases of the body-centered tetragonal lattice, and attempted to account for the author's experimental results by assuming that the mechanism of the transformation is a continuous variation of the axial ratio. This is the simplest and most obvious explanation, and seems to contain some element of truth. However, it does not account for all of the facts, and after going over all of the data we concluded that the actual mechanism was probably more complex. Mr. Bain in his discussion called attention to the weakest point of such an explanation. He said, "There could scarcely be a great preponderance of the tiny grains which would stop their internal atomic reorganization at a specific point,—" The experimental facts are that for a 1.50% C steel, distinct lines were obtained for an axial ratio of 1.06, or in other words that a great preponderance of the tetragonal lattice was at that specific point.

The facts could be explained much better by assuming that the tetragonal lattice with an axial ratio of 1.06 is formed in a discontinuous manner, and that a continuous change may then take place between the axial ratios of 1.06 and 1, or may be suppressed to a greater or less extent. However, the data are not sufficient to warrant any definite conclusion as to the exact nature of the tetragonal lattice, and, as was stated in the

¹Prof. Boylston refers to the cracking of the slide which Mr. Bain used in discussing Mr. Fink's paper. This slide is reproduced as Fig. 2 in Mr. Bain's discussion.

paper, it seems that measurements on steel at elevated temperatures are prerequisite to such a conclusion.

As to Professor Boylston's suggestion that the tetragonal structure might account for the A_2 point, it should be borne in mind that Westgren found no change in the crystal structure of iron at the A_2 point. Therefore it would seem that, at least in the absence of carbon, the change at A_2 is not accompanied by a change in the distribution of the atoms.

